

CHARACTERIZATION OF MICROSTRUCTURE OF ASPHALT, AND CORRELATION WITH THEIR PERFORMANCE

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Introduction

Asphalt is a very complex mixture; even within a given grade the composition may vary significantly depending upon both the source of the crude and the refining process. Although tremendous efforts have been devoted to characterize asphalt, microstructure of asphalt remains to be defined. In particular a routine technique which quantifies the components controlling the long term behavior of an asphalt cement is required. In our laboratory, eight asphalt samples with grades ranging from 10 to 30 from four different sources were examined. The molecular structure of the asphalts was characterized quantitatively using NMR and FTIR techniques. Differential scanning calorimetry (DSC) was employed to estimate the crystallinity, and rheological properties of the asphalts were studied by dynamic mechanical analysis (DMA). Our goal is to achieve an understanding the relaxation mechanisms of asphalt under load at the molecular level.

Characterization of Asphalt Samples

NMR and FTIR Characterization of Asphalt The application of NMR to analysis of asphalt samples is well established [1-3]. Samples were dissolved in deuterated chloroform at a concentration of 10% (w/v), spectra were measured using a Bruker 200 MHz FTNMR. A relaxation agent, $\text{Cr}(\text{acac})_3$, 12 mg/ml, was added to the ^{13}C nmr samples. Using an interpulse time of six seconds and more than 8000 scans, reliable quantitative spectra can be obtained [4]. Table 1 summarizes the observations on our eight samples from the nmr measurements.

It is known that methine structures, especially those attached directly to aromatic ring [5], are mainly responsible for oxidation of asphalt, a major cause of pavement failure. We identified the specific aliphatic carbon types in terms of methyl (8), methylene (19) and methine (6) structures with DEPT technique of ^{13}C nmr (table 2). Comparison of DEPT nmr spectra with broadband nmr spectrum at aromatic band region (100-160 ppm) reveals that no aromatic carbons coupled to hydrogen appears at chemical shifts greater than 131 ppm. The large number of distinctive resonances emphasizes the complexity of the asphalts and suggests that correlating nmr analyses to asphalt chemical and physical properties will be very difficult.

Asphalt samples, 5% (w/v) chloroform solution in 1 mm cell were examined by quantitative FTIR using a Perkin Elmer 1700 FTIR. The overlapped peaks in 1550 - 1800 cm^{-1} were resolved by curve fitting program (figure 1) based on the work of J. C. Petersen and his colleagues [6]. The results (Table 1) show significant differences in composition between asphalt samples of the same grade. Thus comparison of asphalt properties based simply on the grade is rather imprecise.

Crystallinity of Asphalt Linear paraffins present in asphalt readily crystallize. The relative crystallinity of a given asphalt can be measured by DSC [7,8]. We used DSC to estimate the relative volume of the crystalline phase in each of the asphalt samples. A Seiko DSC 220C calibrated for temperature and enthalpy with indium was employed for the measurement. The DSC was conducted on ≈ 10 mg samples sealed in an aluminum sample pan using an empty aluminum sample pan with cap as a reference. Initially each sample was cooled at 3 C/min to -45 C and then heated at 3 C/min. The heats of fusion (ΔH_f) observed are listed in Table 3. The percent crystallinity was estimated from this data by assuming that completely crystallized hydrocarbons in an asphalt matrix exhibit an average enthalpy of 200 J/g (8).

Glass Transition Processes in Asphalt

The glass transition temperature is a very important property to most organic materials not only because it limits practical applications but also because it can provide valuable information about microstructure of a material. We believe that DMA is the best technique to determine T_g both in terms of accuracy and correlation with service conditions of asphalt on the road.

Molded asphalt bars, 20 x 9.495 x 1.64 mm (l x w x t) were mounted in a Seiko DMS 110; each sample was run in bending mode at cooling rate of 1 C/min at single frequency. Operation at single frequency over each temperature range yields more reproducible data than attempting to obtain multifrequency data in a single run. Since multiple runs are required establishing the relationship between frequency and temperature is very time consuming. The T_g was identified as the temperature corresponding to the maxima of loss modular E'' at each frequency. If the T_g is plotted against corresponding frequency based on an Arrhenius equation, an activation energy for the relaxation process can be computed. Table 4 summarizes T_g s and the calculated activation energies, E_a , for our asphalt samples.

Scrutiny of table 4 reveals that asphalts with the same grade can exhibit very different T_g 's, e. g., compare ACC and ACD. An asphalt with a higher grade may have the same or even lower T_g than that of an asphalt with lower grade. Another interesting thing to note is that the values of active energy for the transition process of the asphalt samples are close enough to be considered constant; an average active energy of 9.4 kcal/mol with a standard deviation of ± 0.4 kcal/mol is observed. B. Brule et. al. [8] measured T_g of four asphalt samples with DMA at eight different frequencies from 0.015 to 7.3 Hz, a lower range of frequencies than we employed. We calculated the values for E_a from Brule's data: the results for the four samples are 9.6, 9.3, 9.3 and 8.4 kcal/mol, respectively, which are consistent with our results. The activation energy in this context is an energy barrier separating two set conformations which are in equilibrium. The height of the barrier determines the temperature dependency of wriggling rate. Thus, the constant activation energies imply that the molecular structures responsible for relaxation in each sample are the same. Previous authors [8, 9, 10] have examined fractionated asphalt samples and have shown that only saturates and aromatic fractions contribute to the glass transition. We determined the activation energy of low density polyethylene (LDPE) T_g to be 9.9 kcal/mol, which is very close to that of asphalt. Hence, we postulate that

only those segments primarily composed of aliphatic units are wriggling in the glass transition process.

Imposition of a larger strain (1 %) on the asphalt samples at 50 Hz in DMA experiments will induce cracking at a specific temperature during the cooling. The temperature, called cracking temperature (T_c), can be used to estimate the low temperature cracking resistance of asphalt. The cracking temperature (T_c) is listed in Table 4. Note that all asphalt samples cracked at temperature above their T_g at 50 Hz, which implies T_g measured at this frequency can be considered the limit of brittle temperature of asphalt. In five of the eight cases the asphalt sample cracked at temperature within 4° of its T_g , however sample ACC cracked 11.5° above its T_g . The reason behind this deviation is not clear, but we believe it is related to the morphology of the asphalt. Comparing the data on relative crystallinity of the asphalt samples with T_c (table 3), one observes the sample having exhibiting the highest T_c is the most crystalline. There is a general inverse correlation between the extent of crystallinity and the cracking temperature.

Viscous Flow Process of Asphalt

Flow curves of each asphalt samples were measured with a Bohlin CS rheometer using a cone and plate mode from 5° to 150°C . Initial Newtonian viscosities at different temperatures were determined. At temperatures well above the glass transition temperature, the viscosity is primarily governed by the energy required for a molecule to jump from one site to an adjacent site. The dependence of viscosity on temperature follows the Arrhenius equation [11]. Figure 2 is an example of the Arrhenius plot of the viscosity versus temperature for asphalt. One observes that the curve is basically comprised of two linear regions with a single inflection point. The different slopes imply that the energy barrier of the flow process changed at certain temperature, called the onset temperature T_o , where a significant change in interaction between molecules occurred. The T_o 's determined for each asphalt samples are listed in table 5. The molecular nature of the activation energy change has not experimentally confirmed at this point, but we speculate that dissociation of aromatic π -complexes must contribute to the change in molecular interaction. In addition, polar aromatics may interact to form of a three dimensional network that extends throughout asphalt.

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Table 1 NMR and FTIR Characterization of Asphalt Composition

Sample Source	ACA Calumet	ACB Calumet	ACC Exxon	ACD Exxon	ACE South-land	ACF South-land	ACG Texaco	ACH Texaco
Grade	AC-10	AC-20	AC-10	AC-20	AC-10	AC-20	AC-20	AC-30
Arom H%	5.5	6.1	6.9	6.0	6.3	6.8	7.1	5.7
Arom C%	28.2	30.4	37.3	34.1	33.4	33.7	34.0	24.5
Linear Aliph%	41.8	41.6	22.5	21.8	19.5	21.2	22.3	23.2
Phenolics*	0.0086	0.0058	0.0069	0.003	0.012	0.0093	0.0036	0.004
Pyrolics*	0.0142	0.0112	0.0225	0.0135	0.0137	0.014	0.0145	0.0137
Carboxyl Acid*	0.109	0.0828	0.0318	0.021	0.0220	0.0311	0.0242	0.0324
Ketone*	0.133	0.13	0.0275	0.0195	0.0796	0.043	0.027	0.0362
Quinolone*	0.0412	0.0298	0.0269	0.027	0.023	0.0238	0.0175	0.0109
Sulfoxide*	0.0022	0.001	0.0014	0.0036	0.0043	0.004	0.0008	0.0015

* in mmol/g asphalt.

Table 2 Types of Aliphatic Carbons in Asphalt

Structure Type	Chemical Shifts, ppm
CH ₃	10.8, 11.4, 14.1, 14.4, 19.2, 19.7, 20.3, 23.0
CH ₂	20.1, 21.6, 22.7, 24.5, 25.2, 26.7, 27.1, 27.4, 28.6, 29.4, 29.7, 30.1, 31.9, 33.7, 34.8, 37.1, 37.4, 39.1, 39.4
CH	28.0, 32.8, 34.4, 38.8, 40.2, 46.0

Table 3 Heat of Fusion (ΔH_f) of the Asphalt Samples

Sample	ACA	ACB	ACC	ACD	ACE	ACF	ACG	ACH
ΔH_f (J/g)	7.7	7.8	8.5	9.2	5.8	8.6	11.3	9.6
% crystall.*	3.85	3.9	4.25	4.6	2.9	4.3	5.65	4.8
T _c , °C	-12	-9	-3	-5	-20	-10	0	-3

* Average entropy for 100 % crystalline = 200 J/g (8)

Table 4 Glass Transition Temperature (T_g) from E", Active Energy (E_a) of the Transition and Cracking Temperature (T_c) of Asphalts

Asphalt	1 Hz	10 Hz	50 Hz	E _a (kcal/mol)	T _c
ACA	-23.0°C	-17.8°C	-13.3°C	9.8	-12°C
ACB	-24.9°C	-17.6°C	-14.5°C	8.8	-9°C
ACC	-19.6°C	-17.6°C	-14.5°C	10.0	-3°C
ACD	-14.9°C	-9.9°C	-4.1°C	9.4	-5°C
ACE	-32.2°C	-26.6°C	-22.5°C	9.0	-20°C
ACF	-23.2°C	-18.8°C	-13.8°C	9.5	-10°C
ACG	-16.5°C	-10.5°C	-6.1°C	9.7	0°C
ACH	-16.0°C	-9.6°C	-5.1°C	9.2	-3°C

Table 5 Onset Temperature (T_o) of the Arrhenius Plot of Viscosity ver. Temperature

Sample	ACA	ACB	ACC	ACD	ACE	ACF	ACG	ACH
T _o °C	74	72	63	74	86	75	70	71

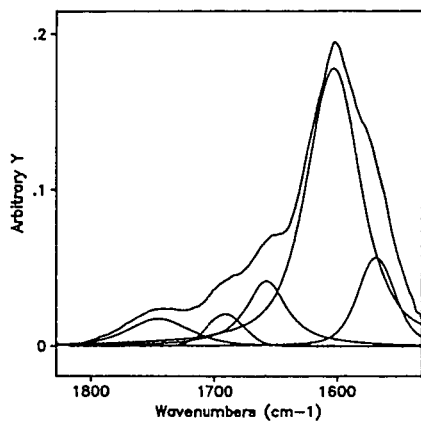


Figure 1 Deconvolution of Overlapped Peaks in a FTIR Spectrum.

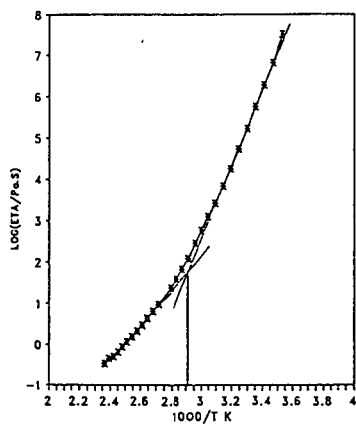


Figure 2 An Arrhenius Plot of Initial Newtonian Viscosity versus Temperature.